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An adhesive bonding approach by hydrogen silsesquioxane for silicon carbide-based LED applications

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ABSTRACT

We report an adhesive bonding approach using hydrogen silsesquioxane (HSQ) for silicon carbide (SiC) samples. A hybrid light-emitting diode (LED) was successfully fabricated through bonding a near-ultraviolet (NUV) LED grown on a commercial 4H-SiC substrate to a free-standing boron-nitrogen co-doped fluorescent-SiC epi-layer. The bonding quality and the electrical performance of the hybrid LED device were characterized. Neither voids nor defects were observed which indicates a good bonding quality of the proposed HSQ approach. A strong warm white emission was successfully obtained from the hybrid LED through an electric current injection of 30 mA.

1. Introduction

Silicon carbide (SiC) has become a popular industrial material in the last decades and has been extensively employed in various applications including waveguides, biosensors and light-emitting diodes (LEDs) thanks to its excellent optical, thermal and electrical properties [1–3]. Particularly, in recent years, there has been increased attention to SiC as a luminescent material in the application of white LEDs. Generally, the most common commercial white LED is made by combining a GaN-based blue LED chip with a coating of yellow phosphors such as cerium-doped yttrium aluminum garnets which contains rare-earth elements [4,5]. However, the utility of this type of white LED is limited by the degraded phosphor performance and the decreased abundance of rare-earth elements. A promising alternative way to fabricate white LEDs combining a near-ultraviolet (NUV) LED with a donor and acceptor co-doped SiC substrate has been proposed [5]. This white LED does not contain any rare-earth element. Two adjacent fluorescent-SiC (f-SiC) epi-layers, one doped by nitrogen (N) and boron (B) and the other one doped by N and aluminum (Al), are employed as the wavelength-conversion materials while the NUV LED is used as the excitation source to the f-SiC epi-layers [5–8].

One fabrication approach to realize this f-SiC based white LED is to combine the NUV LED and the f-SiC epi-layers through adhesive bonding employing an intermediate adhesive layer. Its advantages

include low bonding temperatures, insensitivity to surface topography, resilience to stress and mechanical vibrations and uniform load distribution over a wide area, which makes itself extremely attractive in applications such as three-dimensional integrated circuits, advanced packaging, microfluidics and fiber-optic assemblies [9–14]. In comparison, for fusion bonding techniques, two opposing surfaces are required to be in sufficiently close contact in order to form covalent- or van der Waals bonds, which are the most important bonding mechanisms to take place. Generally, the distance between atoms from the two surfaces to be bonded should be less than 0.5 nm, which makes it difficult to fusion bond surfaces with a large roughness [9]. In this case, flowable adhesives can be applied in between the surfaces to pave the roughness hence bring the atoms of adjacent surfaces into sufficient vicinity to generate the van der Waals bond, which is the basic mechanism in adhesive bonding [9–11]. Although the adhesive bonding is easy to operate and less critical on surface roughness, high transparency of the adhesive bonding material in the NUV range is indispensable to maximize the excitation NUV light propagating to the f-SiC epi-layers.

Hydrogen silsesquioxane (HSQ), which belongs to the inorganic compounds, is commercially available in methyl isobutyl ketone (MIBK) as Fox (flowable oxide). It is widely used in micro- and nano-engineering applications, e.g., as a high-resolution negative electron beam resist [15], as molding material in nanoimprint lithography [16] or as mask in dry etching processes [17]. Furthermore, it is also

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employed as an intermediate material in bonding processes. Successful cases have been carried out for materials including silicon, GaN and AlGaIn [18–23]. Compared to the reported transmittance of the widely used BCB or SU-8 in adhesive bonding, HSQ shows more advantageous in the NUV range with higher and more uniform transmittance [24–27]. Therefore, adhesive bonding by HSQ is a promising candidate for the fabrication approach of f-SiC based white LEDs.

According to the best of our knowledge, no research results have been reported on the application of the HSQ adhesive bonding in SiC-related processes. In this work, an HSQ method for bonding a NUV LED to a free-standing f-SiC epi-layer is presented. After a successful bonding process, a hybrid LED is obtained. The bonding quality and the electrical properties of the hybrid LED are characterized and analyzed to prove that HSQ bonding can be applied in future fabrication of f-SiC based white LEDs.

2. Experimental details

2.1. Growth of the NUV LED and the free-standing f-SiC epi-layer

The GaN-based NUV LED epi-layers were grown on a (0001) 2 in. 4H-SiC substrate by metal-organic chemical vapor deposition (MOCVD) (Cruis I, Aixtron, Germany). The grown LED epi-layer consists of a 3.6 μm thick AlGaIn (5% Al) buffer layer, a 2 μm thick Si-doped n-AlGaIn (7% Al) layer, nine periods of InGaIn (3% In)/AlGaIn (5% Al) MQWs, and finally a 85 nm thick Mg-doped p-AlGaIn (2%) layer and a 32 nm thick Mg-doped p-GaN layer. The free-standing 200 μm B-N co-doped 6H-SiC (f-SiC) epi-layer was grown on a 6H-SiC (0001) substrate with 1.4° off-axis by a fast sublimation growth process [6,7]. After growth, the 6H-SiC substrate was polished away. The roughness (arithmetic mean height) measured by vertical scanning interferometry (VSI) of a PLU NEOX 3D Optical Profiler (Sensofar, Terrassa, Spain) is around 100 nm for the backside (the polished side to be bonded) of the free-standing f-SiC epi-layer while it is around 10 nm for the 4H-SiC substrate of the NUV LED.

2.2. HSQ bonding of the NUV LED and the free-standing f-SiC epi-layer

The bonding process of the NUV LED and the f-SiC epi-layer is shown in Fig. 1. Both samples were cleaned by immersion in acetone for 10 min. Next, HSQ (XR-1541, Dow Corning Corporation) layers with a thickness of around 230 nm were spun on both the 4H-SiC substrate of the NUV LED and the polished backside of the free-standing f-SiC epi-layer. Then, the samples were placed on hotplates for baking at 150 °C for 1 min followed by another baking at 200 °C for 1 min to drive out the solvent. Afterwards, the NUV LED and the f-SiC epi-layer were placed on a holder with the surfaces covered by the HSQ layers in contact.

During the bonding in a Süß SB6 wafer bonder, firstly, vacuum pumping was carried out after the sample surfaces were in contact. Thereafter, the temperature was heated up to 400 °C under vacuum (10^{-4} mbar) with a ramping rate of 15 °C/min. Then, at 400 °C, a force was applied to the samples by a piston for 1 h. The effective bonding

pressure acting on the bond interface was around 250 N/cm². In the end, the sample was cooled down with a ramping rate of 10 °C/min. After successful bonding, a diamond pen was used to expose the n-AlGaIn layer of the NUV epi-wafers and indium spheres were added to the p-type and n-type surfaces, respectively, for electric current injection.

2.3. Characterization

The transmittance of the HSQ layer was measured by a 6 in. integrating sphere system (Gooch & Housego, Ilminster, UK) assisted with a Xenon lamp and a CAS 140 B optical spectrometer (Instrument Systems, Munich, Germany). The measurement was carried out on a test sample where HSQ was spun on top of a pure sapphire substrate. The cross section of the bonded SiC samples with the HSQ interlayer was inspected by a Supra 40 VP scanning electron microscope (SEM) (Zeiss, Oberkochen, Germany) at 5 kV. The emission from the f-SiC side was collected by a large-core optical fiber coupled to the CAS 140 B optical spectrometer. The electric current injection to the NUV LED was carried out by a Model 2450 Interactive SourceMeter instrument system (Keithley, Solon, Ohio, USA).

3. Results and discussion

Fig. 2(a) shows the transmittance spectrum of a 230 nm HSQ layer after normalization of the 86% transmittance of the sapphire substrate. Unlike the sharp transmittance drop of SU-8 in NUV region [26], the transmittance of HSQ appears quite uniform in the measured wavelength range from 370 to 420 nm. At 390 nm, which is the peak wavelength of the employed NUV LED, the transmittance is 98% for the 230 nm HSQ layer. Then the transmittance of a 460 nm HSQ layer on sapphire can be estimated to be around 96% resulting from $98\% \times 98\%$. The 96% transmittance at 390 nm is comparable to the HSQ transmittance shown in Ref. [25]. It confirms the possibility of using HSQ as the adhesive bonding material in the NUV LED-related application due to its high transparency.

Fig. 2(b) shows the cross-section of the cleaved interface between the NUV LED and the f-SiC epi-layer inspected by SEM. As shown in the figure, two layers of 230 nm HSQ, which results in a total thickness of 460 nm, are in contact with the upper f-SiC epi-layer and the lower 4H-SiC substrate of the NUV LED. The HSQ and the SiC surfaces are intimately combined without delamination, which suggests a good adhesion of the 460 nm HSQ interlayer to both the 4H-SiC surface and the surface of the free-standing f-SiC epi-layer. No voids and defects at the HSQ/SiC or HSQ/HSQ interfaces were observed indicating good bonding quality by the HSQ approach.

Fig. 3(a) shows a photograph of the hybrid LED fabricated by HSQ bonding, i.e., with the HSQ intermediate layer embedded in it. In the figure, the indium spheres were added to the NUV LED upper surface as metal contacts for electric current injection and the free-standing f-SiC epi-layer is beneath the NUV LED chip. No voids and defects were observed by shining white light through the hybrid LED demonstrating again the good bonding quality by HSQ. Letters in the background

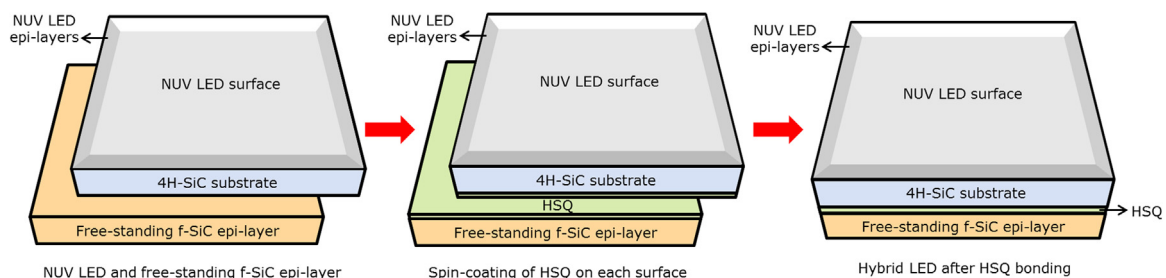


Fig. 1. Schematic illustration of the bonding process of a NUV LED to a free-standing B-N co-doped f-SiC epi-layer assisted with HSQ layers spun on both SiC surfaces.

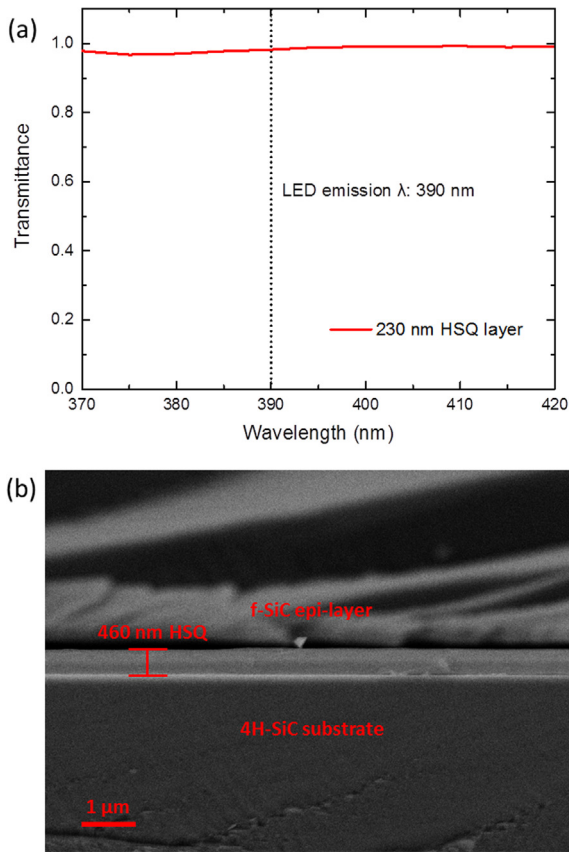


Fig. 2. (a) Optical transmittance spectrum of a 230 nm HSQ layer after normalization of the sapphire substrate in a wavelength range of 370–420 nm. (b) SEM inspection of the cross section of the bonded stack using 460 nm HSQ in between showing no voids.

indicate the white light transparency of the hybrid LED which confirms the feasibility of using white light to visualize the defects.

Fig. 3(b) shows a schematic illustration of the hybrid LED fabricated by bonding after exposing the n-AlGaIn of the NUV LED on the top by a diamond pen. Then, electric current can be injected by pressing probes against the indium spheres added on the surfaces. Here, indium spheres are applied on the sample as contacts since this is an efficient way to test the feasibility of this HSQ bonding approach in hybrid SiC based LED fabrication. In the future, a standard hybrid LED device can be fabricated on the bonded sample through formations of mesas, current spreading layers and metal pads.

The EL emission was successfully obtained for the hybrid LED as shown in Fig. 4. Fig. 4(a) shows a photograph with electric current injection under natural ambient illumination, which was taken from the backside of the hybrid LED (the f-SiC epi-layer side). The hybrid LED was placed on a transparent glass slide in contact with the f-SiC epi-layer while the NUV LED on the top was connected to the probes. Indium spheres added on the top of the hybrid LED can be observed through the bonded NUV LED and f-SiC epi-layer. One probe was connected to the indium sphere on the n-type surface while the other one was connected to the indium sphere on the p-type surface. An electric current injected into the hybrid LED at 30 mA produced NUV emission which excited B-N co-doped f-SiC epi-layer. Finally, a warm white emission, which can be seen in the photograph of Fig. 4(a), was obtained.

Fig. 4(b) shows the EL spectra of the solely NUV LED before bonding (the upper curve) and the hybrid LED after bonding (the bottom curve) measured from the backside at 30 mA (the f-SiC epi-layer side for the hybrid LED). The NUV LED before bonding presents a peak wavelength around 390 nm. After bonding, the emission of the f-SiC epi-layer by the

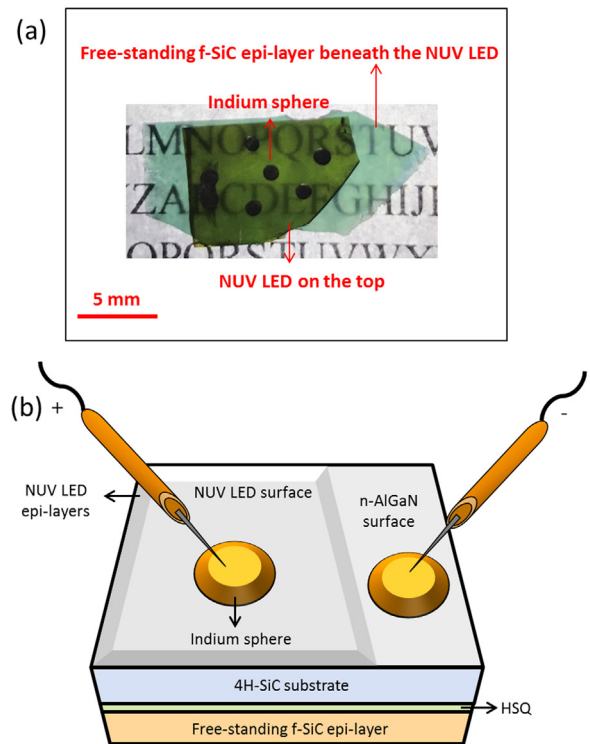


Fig. 3. (a) Photograph of the hybrid LED with the HSQ intermediate layer embedded in it. (b) Schematic illustration of the hybrid LED with indium sphere on the NUV LED for electric current injection through probes.

excitation of the NUV photons can be clearly observed for the hybrid LED showing a peak emission wavelength around 550 nm, which is consistent with the expectation [5,7].

Besides, as shown in Fig. 4(b), in comparison with the 390 nm peak wavelength of the NUV LED before bonding, the NUV peak wavelength shifts to around 405 nm after passing through hybrid LED. This can be explained by the inter-band absorption of the 6H-SiC, which absorbs photons possessing wavelengths shorter than around 408 nm [28,29]. Hence, the long-wavelength photons (blue photons) can pass through the B-N co-doped 6H-SiC epi-layer leading to red-shift of the peak wavelength in the EL of the hybrid LED. In the end, the blue photons combined with the 550 nm-centered emission from the f-SiC epi-layer result in a warm white light as observed in Fig. 4(a).

Furthermore, the performance of the hybrid LED can be further optimized. The 400 μm thick 4H-SiC substrate has a strong absorption in a wavelength range up to 387 nm according to its 3.2 eV optical bandgap. The NUV light generated by LED epi-layers on top has an emission wavelength of 390 nm, which will be partially absorbed by the 4H-SiC substrate. By employment of a thinner or more transparent SiC substrate and a NUV LED with longer emission wavelength, a hybrid LED with stronger EL intensity can be expected.

4. Conclusions

In summary, an adhesive bonding approach using HSQ was employed to successfully bond a NUV LED grown on a 4H-SiC substrate to a free-standing B-N co-doped f-SiC epi-layer. No voids were observed at the HSQ/SiC or HSQ/HSQ interfaces indicating a good bonding quality by this method. Strong EL emission of the hybrid LED was obtained by electric current injection at 30 mA. The NUV emission centered at 390 nm from the NUV LED on the top excites the bottom f-SiC epi-layer to generate emission centered at the wavelength of 550 nm finally presenting a warm white emission. In the future, the white light quality can be improved by employing an extra Al-N co-doped blue-emitting f-

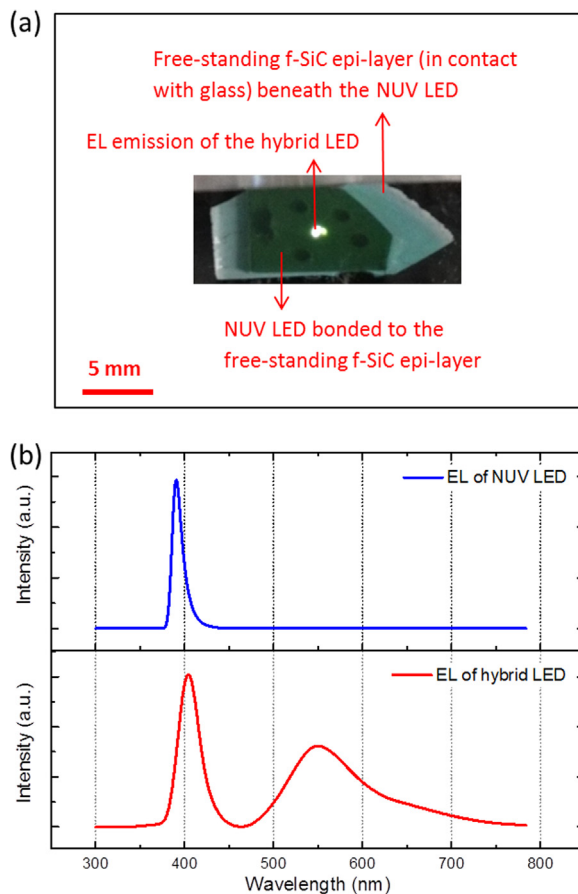


Fig. 4. (a) Photograph of the hybrid lighting LED from backside with electric current injection at 30 mA. (b) The EL spectra of the NUV LED before bonding and the hybrid LED measured from the backside at 30 mA.

SiC epi-layer. From this it can be concluded that, HSQ bonding could be an effective approach in the SiC-based LED applications including the future fabrication of white LEDs based on B-N and Al-N co-doped f-SiC epi-layers.

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References

- [1] A. Oliveros, A. Guiseppe-Elie, S.E. Sadow, Silicon carbide: a versatile material for biosensor applications, *Biomed. Microdevices* 15 (2) (2013) 353–368.
- [2] X. Tang, K. Wongchotigul, M.G. Spencer, Optical waveguide formed by cubic silicon carbide on sapphire substrates, *Appl. Phys. Lett.* 58 (9) (1991) 917–918.
- [3] H.Y. Xu, X.F. Chen, Y. Peng, M.S. Xu, Y. Shen, X.B. Hu, X.G. Xu, Progress in research of GaN-based LEDs fabricated on SiC substrate, *Chin. Phys. B* 24 (6) (2015) 067305.
- [4] S. Nakamura, S. Pearton, G. Fasol, *The Blue Laser Diode: The Complete Story*, Springer Science & Business Media, Berlin, 2013.
- [5] S. Kamiyama, T. Maeda, Y. Nakamura, M. Iwaya, H. Amano, I. Akasaki, H. Kinoshita, T. Furusho, M. Yoshimoto, T. Kimoto, J. Suda, J. Suda, A. Henry,

- I.G. Ivanov, J.P. Bergman, B. Monemar, T. Onuma, S.F. Chichibu, Extremely high quantum efficiency of donor-acceptor-pair emission in N-and-B-doped 6H-SiC, *J. Appl. Phys.* 99 (9) (2006) 093108.
- [6] H. Ou, Y. Ou, A. Argyraki, S. Schimmel, M. Kaiser, P. Wellmann, M.K. Linnarsson, V. Jokubavicius, J. Sun, R. Liljedahl, M. Syväjärvi, Advances in wide bandgap SiC for optoelectronics, *Eur. Phys. J. B* 87 (3) (2014) 58.
- [7] Y. Ou, V. Jokubavicius, S. Kamiyama, C. Liu, R.W. Berg, M. Linnarsson, R. Yakimova, M. Syväjärvi, H. Ou, Donor-acceptor-pair emission characterization in N-B doped fluorescent SiC, *Opt. Mater. Express* 1 (8) (2011) 1439–1446.
- [8] M. Syväjärvi, J. Müller, J.W. Sun, V. Grivickas, Y. Ou, V. Jokubavicius, P. Hens, M. Kaiser, K. Ariyawong, K. Gulbinas, P. Hens, R. Liljedahl, M.K. Linnarsson, S. Kamiyama, P. Wellmann, E. Spiecker, H. Ou, Fluorescent SiC as a new material for white LEDs, *Phys. Scr. T148* (2012) 014002.
- [9] F. Niklaus, G. Stemme, J.Q. Lu, R.J. Gutmann, Adhesive wafer bonding, *J. Appl. Phys.* 99 (3) (2006) 031101.
- [10] B.G. Yacobi, S. Martin, K. Davis, A. Hudson, M. Hubert, Adhesive bonding in microelectronics and photonics, *J. Appl. Phys.* 91 (10) (2002) 6227–6262.
- [11] F. Niklaus, H. Andersson, P. Enoksson, G. Stemme, Low temperature full wafer adhesive bonding of structured wafers, *Sens. Actuators A Phys.* 92 (1–3) (2001) 235–241.
- [12] F. Bu, Q. Ma, Z. Wang, Delamination of bonding Interface between benzocyclobutene (BCB) and silicon dioxide/silicon nitride, *Microelectron. Reliab.* 65 (2016) 225–233.
- [13] B. Bilenberg, T. Nielsen, B. Clausen, A. Kristensen, PMMA to SU-8 bonding for polymer based lab-on-a-chip systems with integrated optics, *J. Micromech. Microeng.* 14 (6) (2004) 814.
- [14] S. Li, C.B. Freidhoff, R.M. Young, R. Ghodssi, Fabrication of micronozzles using low-temperature wafer-level bonding with SU-8, *J. Micromech. Microeng.* 13 (5) (2003) 732.
- [15] St. Trellenkamp, J. Moers, A. Van der Hart, P. Kordoš, H. Lüth, Patterning of 25 nm-wide silicon webs with an aspect ratio of 13, *Microelectron. Eng.* 67 (2003) 376–380.
- [16] Y. Chen, J. Tao, X. Zhao, Z. Cui, A.S. Schwanecke, Ni.I. Zheludev, Nanoimprint lithography for planar chiral photonic meta-materials, *Microelectron. Eng.* 78 (2005) 612–617.
- [17] D. Lauvernier, S. Garidel, C. Legrand, J.P. Vilcot, Realization of sub-micron patterns on GaAs using a HSQ etching mask, *Microelectron. Eng.* 77 (3–4) (2005) 210–216.
- [18] K.K. Ryu, J.W. Chung, B. Lu, T. Palacios, Wafer bonding technology in nitride semiconductors for applications in energy and communications, *ECS Trans.* 33 (4) (2010) 125–135.
- [19] H. Chen, R.E. Tecklenburg, Characterization of low and intermediate molecular weight hydrogen silsesquioxanes by mass spectrometry, *J. Am. Soc. Mass Spectrom.* 17 (10) (2006) 1438–1442.
- [20] J.W. Chung, E. Piner, T. Palacios, "N-face GaN/AlGaN transistors through substrate removal," in: *Proceedings of the Device Research Conference, IEEE, 2008*, pp. 199–200.
- [21] J.W. Chung, E.L. Piner, T. Palacios, N-face GaN/AlGaN HEMTs fabricated through layer transfer technology, *IEEE Electron Device Lett.* 30 (2) (2009) 113–116.
- [22] S. Sergeant, M. Arita, S. Kako, K. Tanabe, S. Iwamoto, Y. Arakawa, High-Q AlN photonic crystal nanobeam cavities fabricated by layer transfer, *Appl. Phys. Lett.* 101 (10) (2012) 101106.
- [23] S. Lis, R. Dylewicz, J. Myśliwiec, A. Miniewicz, S. Patela, Application of flowable oxides in photonics, *Mater. Sci. Pol.* 26 (1) (2008) 189–194.
- [24] X. Zhang, O. Adelegan, F.Y. Yamaner, Ö. Oralkan, An optically transparent capacitive micromachined ultrasonic transducer (CMUT) fabricated using SU-8 or BCB adhesive wafer bonding, in: *Proceedings of the Ultrasonics Symposium (IUS), (IEEE International, 2017)*, pp. 1–4.
- [25] T.S. Chang, T.C. Chang, P.T. Liu, S.W. Tsao, F.S. Yeh, Investigation of the low dielectric siloxane-based hydrogen silsesquioxane (HSQ) as passivation layer on TFT-LCD, *Thin Solid Films* 516 (2–4) (2007) 374–377.
- [26] J.N. Kuo, C.C. Hsieh, S.Y. Yang, G.B. Lee, An SU-8 microlens array fabricated by soft replica molding for cell counting applications, *J. Micromech. Microeng.* 17 (4) (2007) 693.
- [27] Q. Wang, A.Z. Zhang, A. Bergström, V.Z. Huo, S. Almqvist, W. Kaplan, J.Y. Andersson, Micro-Optical Elements Functioning in Non-Visible Spectral Range, *Micro-Optics, International Society for Optics and Photonics, Brussels, Belgium, 2010*, p. 771609.
- [28] J.B. Casady, R.W. Johnsonm, Status of silicon carbide (SiC) as a wide-bandgap semiconductor for high-temperature applications: a review, *Solid State Electron* 39 (10) (1996) 1409–1422.
- [29] W. Xie, J.A. Cooper, M.R. Melloch, Monolithic NMOS digital integrated circuits in 6H-SiC, *IEEE Electron Device Lett.* 15 (11) (1994) 455–457.